

April- May 2007

US EPA Region 10

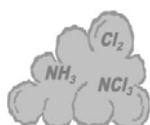
## Inside This Issue

- 1 Chemical Reactivity Hazards
- 3 Government Regulations
- 3 Profile of Reactive Incidents
- 5 The Chemical Reactivity Worksheet
- 6 Sodium Hydrosulfide: Hazardous Reactions and Preventing Harm
- 7 Free On-line Publications on Chemical Reactivity
- 8 NFPA Hazard Rating
- 9 Time-Sensitive Chemicals and Sharing Lessons

## This issue features:

# Chemical Reactivity Hazards (Uncontrolled Chemical Reactions)

Major chemical accidents cannot be prevented solely through regulatory requirements, but by understanding the fundamental root causes, widely disseminating the lessons learned, and integrating these lessons learned into safe operations. It is important that facilities, SERCs, LEPCs, emergency responders and others review the available information on chemical reactivity and take appropriate steps to minimize risk.



Clean Air Act 112(r) 40 CFR 68.65(b) Process safety information ...  
*"Information pertaining to the hazards of the regulated substances in the process... shall consist of at least the following:... reactivity data... thermal and chemical stability data, and hazardous effects of inadvertent mixing of different materials that could foreseeably occur."*

Reactive chemistry incidents continue to occur in the chemical processing industry, and other industries which handle chemicals in their manufacturing processes. Here are some examples:

1

## Explosion and Fire: Napp Technologies, Lodi, New Jersey

An explosion and fire at a manufacturing facility in Lodi, New Jersey caused the death of five responders. The explosion occurred while the company was blending aluminum powder, sodium hydrosulfite, and other ingredients.

Although the material was water reactive, the MSDS for the product advised the use of a "water spray . . . to extinguish fire." The recommendation in the MSDS for "small fires" was to flood with water. However, "small fire" was not defined, the amount of water necessary was not specified, and no information dealt with how to respond to large fires (which can occur during blending processes). The MSDS only described the hazards associated with the blended product. Incident responders needed information on the chemical reactivity hazards during the blending process, which were

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CHEMICAL EMERGENCY PREVENTION  
& PLANNING *Newsletter*  
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significantly different in this case from the hazards associated with the finished product.

## 2

### **Waste Mixing Explosion: Kaltech Industries, New York City**

An explosion occurred at Kaltech Industries, a sign manufacturer in the Chelsea neighborhood of New York City, injuring 36 people seriously enough to seek hospital treatment, including 14 members of the public. The explosion, which was the result of a reaction between waste chemicals, originated in the basement of a mixed-use commercial building and caused damage as high as the fifth floor. The investigation found that Kaltech failed to maintain an OSHA-required hazard communication program and failed to manage hazardous waste in accordance with established EPA regulations.

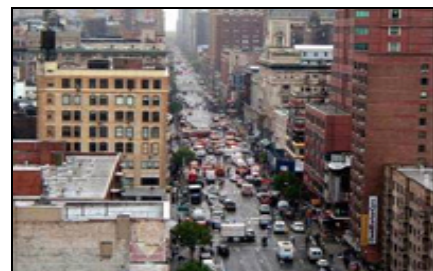


*Runaway chemical reaction  
killed five responders at Napp  
Technologies*

## 3

### **Azinphos Methyl Explosion: Arkansas Warehouse, Arkansas**

A massive explosion and fire occurred at an agricultural chemical facility in eastern Arkansas. Prior to the explosion, employees observed smoke in a back warehouse and evacuated. The facility called local responders and asked for help to control smoldering inside a supersack of azinphos methyl, a pesticide. The local fire department rapidly responded and reviewed the MSDS of the smoldering product. The MSDS lacked information on decomposition temperatures or explosion hazards. The firefighters decided to investigate the building. While they were approaching, a violent explosion occurred. Fragments from a collapsing cinder block wall killed three firefighters and seriously injured a fourth.



*Scene of Kaltech explosion on  
19th Street in Chelsea  
neighborhood of Manhattan*

## 4

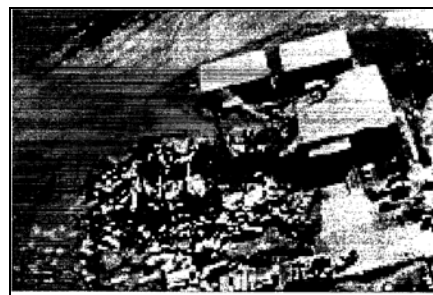
### **Runaway Reaction and Explosion: Georgia-Pacific Resins, Columbus, Ohio**

An explosion occurred in a resins production unit at Georgia-Pacific Resins, Inc. in Columbus, Ohio. The blast was reported to be felt at least 2 miles. As a result of the explosion, one worker was killed and four others injured. Three firefighters were injured during the response.

The explosion also resulted in the release of a large quantity of liquid resin and smaller quantities of other chemicals within the facility. The explosion extensively damaged the plant.

Georgia-Pacific was manufacturing a phenolic resin in an 8000-gal batch reactor when the incident occurred.

The investigation revealed that, contrary to Standard Operating Procedure (SOP), the operator charged the raw chemicals to the reactor at once and turned on the steam to initiate the reaction. (The SOP is to add the chemicals slowly either continuously or as small incremental steps. It is not added all at once). A high temperature alarm sounded and the operator



*View of Arkansas Warehouse  
following explosion that killed  
three firefighters*

turned off the steam. Shortly after, the top of the reactor blew and the sides of the reactor split killing the operator and injuring four other workers. The top landed 400 feet away. The reactor had heated up too fast resulting in a sudden increase in pressure overwhelming the pressure relief valves and the reflux cooling system.

## 5

### Some Landmark Reactive Incidents in History

Chemical reactivity hazards have been involved in some of the most severe industry incidents in history.

Examples are:

- The 2001 massive ammonium nitrate explosion

near Toulouse, France that led to 30 fatalities, 2500 injuries, damage to nearly a third of the city of Toulouse, and the permanent closing of the facility.

*Crater formed  
by explosion  
near Toulouse,  
France*



- The 1984 methyl isocyanate release in Bhopal, India that resulted in more than 2000 fatalities.
- The 1976 runaway reaction at Seveso, Italy that resulted in the contamination of several square miles of land with dioxin. As many as 2000 persons were treated for dioxin poisoning.

(References: EPA Publication; European Commission)

#### Chemical Reactivity Hazards

### Government Regulations

As an example of how chemical reactivity hazards are regulated, the **U.S. Occupational Safety and Health Administration (OSHA) Process Safety Management Standard, 29 CFR 1910.119**, includes a number of "highly reactive" materials in its list of regulated chemicals. The handling of one or more of these substances above its threshold quantity at a fixed facility requires a process safety management (PSM) program to be in place.

Other U.S. federal regulations that have some relation to managing chemical reactivity hazards include the **EPA Risk Management Program (RMP) Rule (40 CFR Part 68)**, **EPCRA Sections 311 and 312**, **RCRA**, and the **OSHA Hazard Communication Standard (29 CFR 1910.1200)**.

Although the EPA RMP Rule does not explicitly cover chemical reactivity hazards, a number of the chemicals covered by the RMP Rule have significant reactivity properties as well as toxic or flammable hazards. **General duty clauses** are included in both OSHA (OSH Act 1970) and Clean Air Act legislation that relate, respectively, to providing a safe workplace and preventing accidental releases of extremely hazardous substances. EPA has provided authority to implement the general duty clause in **Section 112(r)(1) of the Clean Air Act**.

## Profile of Reactive Incidents

The U.S. Chemical Safety and Hazard Investigation Board (CSB) investigated 167 serious incidents involving uncontrolled chemical reactivity that occurred over the 22 year period from January 1980 to June 2001. The investigation results were released in September 2003.

The investigation covered both chemical manufacturing (i.e., raw material storage, chemical processing, and product storage) and other industrial activities involving bulk chemicals, such as storage/distribution, waste processing, and petroleum refining. (Incidents involving transportation, pipelines, laboratories, minerals extraction, mining, explosives manufacturing, pyrotechnic manufacturing, or military uses were excluded, in addition to events involving simple combustion). Only reactive incidents that caused injuries or fatalities, significant property damage, environmental contamination, and offsite evacuation or shelter-in-place were examined.

The investigations revealed the following:

- o The reactive incidents caused an average of six  
- more -

injury-related incidents per year, resulting in an average of five fatalities annually.

- About 66 percent of the 167 incidents occurred in the chemical manufacturing industry.
- Nearly 50 of the 167 incidents affected the public.
- Over 90 percent of reactive incidents involved hazards that are already recognized and documented in published literature.

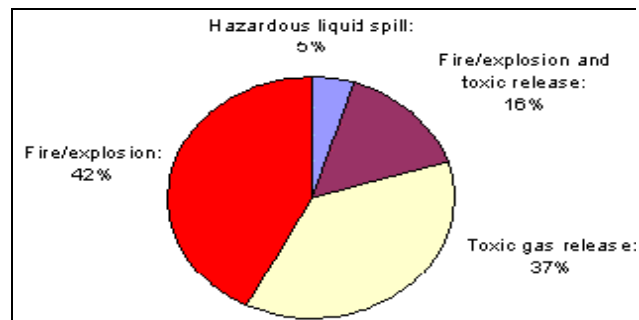


Figure 1: Consequences (Results) of the 167 Reactive Incidents

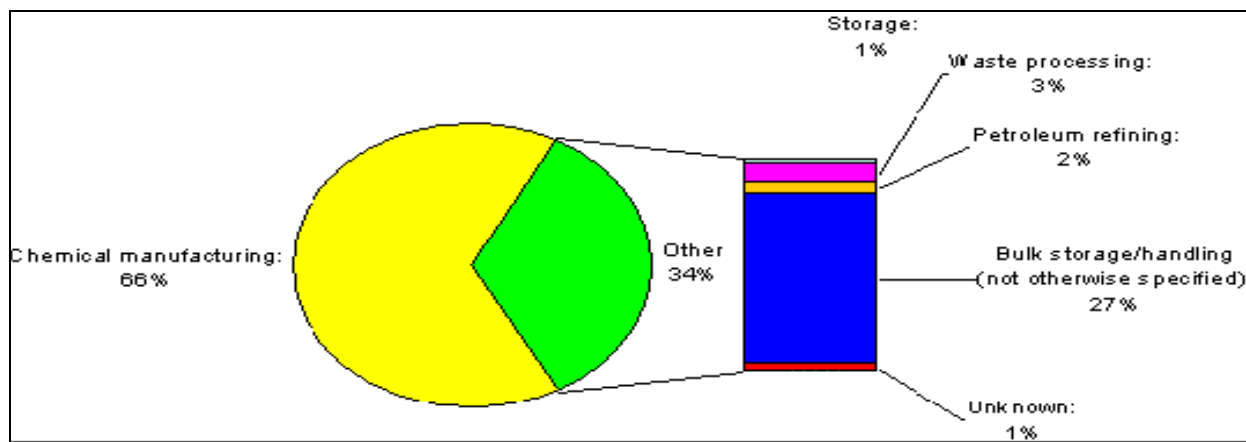


Figure 2: Industry Sector of the 167 Reactive Incidents

EPA reviewed CSB's information and identified the most commonly reported management deficiencies. In order of frequency, the reported management deficiencies are:

- Operating Procedures, Safe Operating Limits and Training
- Hazard Identification and Evaluation
- Human Factors
- Management of Change
- Emergency Relief Equipment and Controls
- Process Design
- Process Knowledge
- Incident Investigation
- Process Hazard Analysis
- Safety Auditing
- Equipment Maintenance

Figures 1 and 2 provide insight into the profile of reactive incidents.

In their report, CSB points to the limited availability of accurate reactive chemical incident data. In spite of these limitations, the data set is useful in identifying areas of management systems that need to be strengthened in order to address the hazards of reactive chemicals. The following are some essential

practices for managing chemical reactivity hazards:

#### ✓ **Communicate and Train On Chemical Reactivity Hazards**

Training activities and materials should incorporate the hazards of chemical reactivity and provide information relevant to workers directing and performing process operations.

#### ✓ **Identify Process Controls and Risk Management Options**

The materials receiving and transfer system should be designed to guard against inadvertent mixing or incorrect handling.

#### ✓ **Manage Process Knowledge**

Technical information pertaining to fire protection, safety, health and environmental protection should be freely exchanged between organizations within industry and by technical societies.

#### ✓ **Conduct a Process Hazard Analysis (PHA)**

Many methods of conducting a PHA are suitable

- more -

for assessing the hazards associated with operation of facilities involving reactive materials or mixtures. Several methods, such as "hazard and operability" and "what-if", rely on a base set of questions for identifying risks. These base sets of questions should be expanded to include aspects that may be unique to reactive chemicals. Additionally, any process change that is made should receive a management of change (MOC) review.

### ✓ **Consider Abnormal Situations**

The severity of many chemical accidents can be attributed to a reluctance to seriously consider all scenarios and to develop an appropriate action plans. Identifying and evaluating deviations that may occur and developing appropriate responses must be thought out before the fact. Possible abnormal situations must be documented and incorporated into instructions and training for operating personnel and for emergency responders. Otherwise, there is likely to be no response or an inadequate one.

### ✓ **Conduct Frequent Audits**

Safety, health and environmental (SHE) audits can serve a number of invaluable functions, including verification that the concepts of reactive chemical hazards are understood by operating personnel and have been built into the operation. The SHE audit may be the last line of defense against an accident. Audits provide an opportunity for input from individuals in all levels of the organizations. Audit teams must also include at least one person with a good understanding of the methods for identifying chemical reactivity hazards. Team members should be familiar with the different elements of a sound management system and be able to determine if each element is functioning as intended. The effectiveness of the training programs and the operating procedures should be a focal point of the audit program.

(References: EPA Pamphlet 550-F-04-005;  
CSB Report "Reactivities Hazards Investigation")

## **Chemical Reaction Software**

# **The Chemical Reactivity Worksheet**

**A** facility making chemical process changes, or even a facility that is merely rearranging chemicals stored at the facility, should be aware of, and consider the compatibility of, the various chemicals that may be stored next to each other at the facility. This is important because the inadvertent mixing of incompatible chemicals can cause fires, explosions, poison gases to form, and other unexpected outcomes. It is important to consider what possible mixing of chemicals might occur in the event of a spill, fire, or hazardous materials incident.

To help understand potential reactions where more than one chemical may be involved in a spill scenario, the Chemical Reactivity Worksheet has been developed. It can be downloaded from the Internet from the website: <http://response.restoration.noaa.gov/chemaids/react.html>

The **Chemical Reactivity Worksheet** is a free program you can use to find out about the reactivity of substances or mixtures of substances (reactivity is the tendency of substances to undergo chemical change). It includes:



- a database of reactivity information for more than 6,000 common hazardous chemicals;
- a way for you to virtually "mix" chemicals like the chemicals in the derailed tank cars shown above to find out what dangers could arise from accidental mixing.

The database includes information about the intrinsic hazards of each chemical and about whether a chemical reacts with air, water, or other materials. It also includes case histories on specific chemical incidents, with references.

The latest version of the Worksheet is version 1.7, released on February 2006. The Worksheet was developed by the Chemical Reactivity Team at the Office of Response and Restoration (OR&R), National Ocean Service, National Oceanic and Atmospheric Administration (NOAA).

(Reference: NOAA)

## Sodium Hydrosulfide:

# Hazardous Reactions and Preventing Harm

Since 1971, reported incidents involving liquid solutions of sodium hydrosulfide (NaHS) have resulted in 32 deaths and 176 injuries, most notably in the leather tanning and pulp and paper industries. The most serious safety concern associated with NaHS is its capacity to produce large amounts of deadly hydrogen sulfide gas (H<sub>2</sub>S) when it reacts with an acid or is exposed to high heat. Despite its pungent rotten egg odor, H<sub>2</sub>S can deaden the nerves that detect odors, thereby preventing those exposed from being able to smell life-threatening airborne concentrations.

## DEFINING THE PROBLEM

NaHS releases highly toxic H<sub>2</sub>S if mixed with an acid or if exposed to excessive heat. Because it is corrosive, it is also potentially harmful to the skin and eyes.

NaHS incidents typically involve the following three elements:

- 1) An inadvertent spill, leak, or mixing, whereby NaHS reacts with an acidic solution to produce H<sub>2</sub>S.
- 2) Absent or inadequate engineering controls, such as ventilation or H<sub>2</sub>S detection devices, coupled with inadequate personal protective equipment (PPE).
- 3) Inappropriate emergency response actions by workers and emergency responders.

The following were identified as the two common management failures during review of catastrophic NaHS-related incidents:

- 1) Failure to identify and mitigate hazards during process system design and engineering.
- 2) Failure to manage hazards that were not controlled through good design and engineering.

## INCIDENT DATA

The Chemical Safety and Hazard Investigation Board (CSB) identified 45 NaHS-related incidents in the United States from 1971 through 2004. Incident data were obtained from EPA, OSHA, and ATSDR databases, as well as industry questionnaires, interviews, and media sources.

Collectively, these incidents resulted in:

- 32 fatalities
- 176 injuries
- 351 medical evaluations
- at least 10 plant or community evacuations

The following causal categories were identified:

- Improper mixing or transfer: 15 (33 percent)
- Spills: 12 (27 percent)
- Mechanical failure: 7 (16 percent)
- Improper maintenance: 6 (13 percent)
- Unknown causes: 5 (11 percent)

## PREVENTING HARM

### ➤ Design to Eliminate Hazards

Interviews and literature reviews with NaHS manufacturers, trade associations, and industry representatives highlighted the following design practices:

- ✓ Always treat sewers as extensions of the process. Do NOT add wastes without analyzing for compatibility with other sewer contents.
- ✓ Separate acid- and NaHS-containing waste streams, or design the system to handle mixing so as to prevent an uncontrolled or otherwise hazardous release of H<sub>2</sub>S.
- ✓ Construct separate containments for NaHS and acid storage containers and process equipment.
- ✓ If waste NaHS and acids are mixed in a sewer, install waste stream/sewer monitors with alarms to warn employees of system upsets or unfavorable acid conditions.
- ✓ Install ventilation systems and H<sub>2</sub>S detectors and alarms at locations where hazardous concentrations may occur (e.g., storage areas and offloading terminals).
- ✓ Design storage tank vents to minimize the potential for worker exposure.
- ✓ Design transfer connections and procedures to prevent inadvertent mixing. Limit access to these connections to trained and authorized personnel through reliable and effective controls, which should include procedures and physical barriers (e.g. locking devices or

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unique fitting configurations).

- ✓ Construct process system components from materials capable of withstanding the corrosivity and temperatures associated with NaHS solutions.

### ➤ Manage Hazards

The following management systems were identified as particularly applicable to NaHS users.

#### ✓ *Communicate Hazards to Employees*

The OSHA HazCom Standard (29 CFR 1910.1200) is based on the simple concept that employees have both a need and a right to know of the hazards associated with chemicals to which they are exposed. They also need to know how to protect themselves from adverse health effects due to chemical exposure. The general requirements of this standard are outlined at <http://www.osha.gov>.

#### ✓ *Provide personal protective equipment*

Facilities should rely on PPE only after conducting a hazard assessment, as required by the OSHA Personal Protective Equipment, General Requirements Standard (29 CFR 1910.132). Employees should participate in the selection of PPE because of the potential for stress and discomfort created by restrictions to movement, vision, and dexterity. Where practical, PPE should be simple to operate and reasonably comfortable to wear for the duration of the exposure.

#### ✓ *Enter confined spaces safely*

Because H<sub>2</sub>S is heavier than air, it tends to concentrate near or below ground level, especially where there is limited air movement. Sump pits, storage and process tanks, valve trenches, and sewers are particularly susceptible to high concentrations of H<sub>2</sub>S and may require atmospheric testing, communications equipment, and standby emergency rescue personnel. OSHA regulates confined spaces in the Permit-Required Confined Spaces Standard (29 CFR 1910.146).

#### ✓ *Handle and store NaHS safely*

The hazards associated with NaHS require employers to establish facility-specific safe handling and storage practices and procedures

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## Free On-line Publications on Chemical Reactivity



### ▪ Chemical Safety Alert: Managing Chemical Reactivity Hazards

Issued: February 2005 (0.04MB) (PDF)

An Environmental Protection Agency (EPA) Alert designed to introduce facilities to the methodology for chemical reactivity hazard management. Go to: [http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/reactive-management-pub.pdf/\\$File/reactive-management-pub.pdf](http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/reactive-management-pub.pdf/$File/reactive-management-pub.pdf)

### ▪ Identifying Chemical Reactivity Hazards Preliminary Screening Method

Issued: May 2004 (0.36MB)(PDF)

An EPA Alert designed to raise awareness of reactive chemical hazards and a method of screening for these hazards. Go to:

[http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/flowchart.pdf/\\$File/flowchart.pdf](http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/flowchart.pdf/$File/flowchart.pdf)

### ▪ Essential Practices for Managing Chemical Reactivity Hazards

The Environmental Protection Agency, the Center for Chemical Process Safety (CCPS), the Occupational Safety and Health Administration (OSHA), the American Chemistry Council, and Synthetic Organic Chemical Manufacturers Association, has made available online the book *Essential Practices for Managing Chemical Reactivity Hazards* (2003). This book, intended for safety managers, chemists, and engineers alike, helps both small and large companies address safe handling, processing and storing of chemicals that might become involved in uncontrolled chemical reactions. For free access to this book, register at the website:

<http://info.knovel.com/ccps/>

### ▪ Reactive Material Hazards - What You Need to Know

Issued: October 2001 (291 KB) (PDF)

CCPS developed this pamphlet to help safety managers, chemists, and engineers determine whether a process could have a chemical reactivity hazard and what they should do. Go to:

<http://www.aiche.org/ccps/>

for both employees and contractors.

### CASE STUDY Powell Duffryn terminal fire, Georgia

On April 10, 1995, the force from an explosion in a solvent storage tank fractured NaHS transfer piping. Up to 300,000 gallons of NaHS spilled and mixed with a similarly large quantity of acidic cleaning solution (see figure below). The NaHS and acid solution tanks were collocated inside an earthen containment.

The reaction released an enormous volume of H<sub>2</sub>S, which caused 337 people to seek medical evaluations and forced 2,000 downwind residents to evacuate. The evacuation lasted more than 30



*Powell Duffryn terminal fire*

days as H<sub>2</sub>S continued to evolve from NaHS-saturated soil.

This incident illustrates the failure of management systems to identify and evaluate the hazards associated with collocating incompatible materials inside a single spill containment.

**New!** New versions of the CAMEO software suite were made available on the EPA/CAMEO website



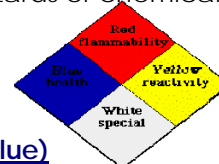
Many chemicals behave in somewhat predictable ways when spilled. The way a spill of gases or liquids will disperse can be "modeled." CAMEO is a comprehensive computer software program that aids in modeling chemical spills. CAMEO also contains basic information on facilities that store chemicals, on the inventory of chemicals at the facility (Tier II) and on emergency planning resources. CAMEO connects the planner or emergency responder with critical information to identify unknown substances during an incident. On February 2007, new versions of the CAMEO software suite were made available on the EPA/CAMEO website.

ALOHA and MARLOT are components of CAMEO software. ALOHA is an air dispersion model used to evaluate hazardous chemical scenarios and determine the likely "footprint" of such spills. MARPLOT is the mapping application. It allows users to "see" their data (e.g., roads, facilities, schools, response assets), display this information on computer maps, and print the information on area maps. The areas contaminated by potential or actual chemical release scenarios also can be overlaid on the maps to determine potential impacts. To download the latest versions, follow the link: (<http://www.epa.gov/oem/cameo/>).

## NFPA Hazard Rating

The hazard rating system described in National Fire Protection Association (NFPA) 704 indicates the *health*, *flammability* and *reactivity* hazards of chemicals.

### Rating Summary



#### Health (Blue)

- 4 – Danger ---- May be fatal on short exposure. Specialized protective equipment required
- 3 – Warning --- Corrosive or toxic. Avoid skin contact or inhalation
- 2 – Warning --- May be harmful if inhaled or absorbed
- 1 – Caution --- May be irritating
- 0 ----- No unusual hazard

#### Flammability (Red)

- 4 – Danger ---- Flammable gas or extremely flammable liquid
- 3 – Warning --- Flammable liquid flash point below 100° F
- 2 – Caution---- Combustible liquid flash point of 100° to 200° F
- 1 ----- Combustible if heated
- 0 ----- Not combustible

#### Reactivity (Yellow)

- 4 – Danger ---- Explosive material at room temperature
- 3 -- Danger --- May be explosive if shocked, heated under confinement or mixed with water
- 2 – Warning --- Unstable, may react violently with water
- 1 – Caution --- May react if mixed with water but not violently
- 0 – Stable ----- Not reactive when mixed with water

#### Special Notice Key (White)

- W ----- Water Reactive
- Oxy ----- Oxidizing Agent

## Time-Sensitive Chemicals and Sharing Lessons



Many chemicals have a 'shelf life', they become unstable or reactive with time in storage. For example, some monomers require inhibitor to prevent polymerization, and, after a period of time, the inhibitor is consumed. The manufacturer of such chemicals will normally provide an "expiration date" for the material, and it is important to use the material or properly dispose of it before that expiration date.

A company had two "near misses" – bulging or ruptured drums – because time sensitive chemicals had been stored too long.

Fortunately nobody was hurt, and damage was minor. The company had a good system for reporting and sharing near misses, and these incidents were shared throughout the organization. Another plant saw the reports, and immediately checked all of the material in the warehouse. They found four drums of the same material which were past the expiration date and had begun to polymerize. Luckily, none of the drums had ruptured. The plant safely discarded the material and a potential explosion or injury was avoided.

### Did You Know?

- Some reactive chemicals must be used by a specified date or they will become unstable.
- Other chemicals can accumulate impurities (such as peroxides) over time and can also become unstable.
- Material Safety Data Sheets (MSDS) should tell you if materials can become unstable with time or need special storage conditions.
- Reporting and investigating "near misses" is an excellent way to prevent future incidents.

### What You Can Do

- Know if chemicals in your workplace can become unstable during storage – check the MSDS, with your safety specialist, or contact the supplier.
- Understand and follow your company's procedure for managing time sensitive materials (make sure you have one!); they should not be stored too long.
- Report all incidents and near misses to help prevent future incidents.
- Share incidents with others so we can all learn from your experience.

(Source: Process Safety Beacon)

*"Major chemical accidents cannot be prevented solely through regulatory requirements, but by understanding the fundamental root causes, widely disseminating the lessons learned, and integrating these lessons learned into safe operations."* – EPA, *Managing Chemical Reactivity Hazards*.

This newsletter provides information on the EPA Risk Management Program, EPCRA and other issues relating to the Accidental Release Prevention Requirements of the Clean Air Act. The information should be used as a reference tool, not as a definitive source of compliance information. Compliance regulations are published in 40 CFR Part 68 for CAA section 112(r) Risk Management Program, and 40 CFR Part 355/370 for EPCRA.